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First-Principles Thermoelasticity of Tantalum at High Pressures

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First-principles thermoelasticity of tantalum at high pressures

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Abstract

The thermoelastic properties of bcc tantalum have been investigated over a broad range of temperatures (up to 12000 K) and pressures (up to 10 Mbar) using first-principles methods that account for cold, electron-thermal, and ion-thermal contributions. Specifically, we have combined *ab initio* all electron electronic-structure calculations for the cold and electron-thermal contributions to the elastic moduli with phonon contributions for the ion-thermal part calculated using model generalized pseudopotential theory (MGPT). For the latter, a summation of terms over the Brillouin zone is performed within the quasi-harmonic approximation, where each term is composed of a strain derivative of the phonon frequency at a particular k-point. At ambient pressure, the resulting temperature dependence of the elastic moduli is in excellent agreement with ultrasonic measurements. The experimentally observed anomalous behavior of C_{44} at low temperatures is shown to originate from the electron-thermal contribution. At higher temperatures, the dominant contribution to the temperature dependence of the elastic moduli comes from thermal expansion. Also, the pressure dependence of the moduli compares well with recent diamond-anvil cell measurements up to 105 GPa. The calculated longitudinal and bulk sound velocities at higher pressure and temperature agree well with data obtained from shock experiments. Additionally, the temperature dependence of the Steinberg-Guinan model is examined for ambient pressure.

Motivation

- **Elastic moduli are fundamental in describing mechanical behavior of materials, like mechanical stability.**

- **Elastic moduli are crucial in large-scale models:**
  - **Steinberg-Guinan strength model**
  - **dislocation models (Yang, Söderlind & Moriarty 2001).**

- **However, temperature effects are ignored many times, but are not always insignificant.**

- **Monte Carlo methods in the past have determined the temperature and pressure dependence of elastic moduli (Greeff & Moriarty, 1999).**

- **Particle-in-cell model based FP-LAPW method (Gülseren & Cohen, 2002) has also been used, specifically for Ta.**

- **Molecular dynamics could also be used to determine the elastic moduli.**

⇒ **We sought a method that would be computationally less expensive.**

⇒ **Here, we shall discuss quasi-harmonic results, however, we in the future intend to include anharmonic effects to the elastic moduli.**

Quasi-harmonic formulation

- **Within the quasi-harmonic approximation, we have determined the individual elastic moduli in the following way (Wallace, 1972).**

- **The Helmholtz free energy of a system in terms of volume (Ω) and temperature (T) is written as,**

$$F(\Omega,T) = \Phi_o(\Omega,T=0) + F_e(\Omega,T) + F_{ion}(\Omega,T)\ .$$

$\Phi_o(\Omega,T=0)$ is static lattice potential.

$F_e(\Omega,T) = U_e - TS_e$ is the electronic thermal contribution, where

$$S_e(\Omega,T) = -k_B \int d\epsilon\, n(\epsilon,\Omega)\{f(\epsilon)ln[f(\epsilon)] - (1-f(\epsilon))ln[1-f(\epsilon)]\}$$

The ion thermal contribution is

$$F_{ion}(\Omega,T) = \sum_\kappa \{\tfrac{1}{2}\hbar\omega_\kappa + k_B T ln[1-exp(-\hbar\omega_\kappa/k_B T)]\}$$

- **From strain derivatives of F, elastic moduli are written as,**

$$C^T_{ijkl} = C^o_{ijkl} + C^e_{ijkl} + C^{ion}_{ijkl}$$

Quasi-harmonic formulation

- **Stress:** $$\tau_{ij} = \frac{1}{V} \frac{\partial F}{\partial \eta_{ij}}\bigg|_{T\eta'}$$

- **Elastic constants:** $$C^T_{ijkl} = \frac{1}{V} \frac{\partial^2 F}{\partial \eta_{ij} \partial \eta_{kl}}\bigg|_{T\eta'}$$

$$\Rightarrow C^T_{ijkl} = C^o_{ijkl} + C^e_{ijkl} + C^{ion}_{ijkl}$$

$$\tau^{ion}_{ij} = -\frac{1}{V} \sum_{\kappa} \hbar\omega_\kappa \, \gamma_{\kappa,ij} (\bar{n}_\kappa + \tfrac{1}{2})$$

$$C^{ion}_{ijkl} = \frac{1}{V} \sum_{\kappa} \hbar\omega_\kappa \left[\xi_{\kappa,ijkl} (\bar{n}_\kappa + \tfrac{1}{2}) - \gamma_{\kappa,ij} \, \gamma_{\kappa,kl} \, \frac{\hbar\omega_\kappa}{k_B T} (\bar{n}^2_\kappa + \bar{n}_\kappa) \right]$$

where $$\gamma_{\kappa,ij} = -\frac{1}{\omega(\kappa)} \frac{\partial \omega(\kappa)}{\partial \eta_{ij}},$$

$$\xi_{\kappa,ijkl} = \frac{1}{\omega(\kappa)} \frac{\partial^2 \omega(\kappa)}{\partial \eta_{ij} \partial \eta_{kl}},$$

and $$\bar{n}_\kappa = [exp(-\hbar\omega_\kappa / k_B T) - 1]^{-1}.$$

$\Rightarrow$ **These derivatives are performed numerically via deformations to the crystal.**

Coupling computational methods

⇒ **Electron thermal contribution is calculated via full potential linear muffin-tin orbital(FP-LMTO) theory (Wills):**

- **non-spherical charge density**
- **spin-orbit interaction**
- **exchange-correlation functional, GGA (Perdew, 1992)**
- **Semi-core states: 5s, 5p, 4f**
- **Valence states: 6s, 6p, 5d, 5f**
- **Electronic temperature is incorporated in the energy and in the electronic entropy by thermal broadening of the electronic density of states with the Fermi-Dirac distribution.**
- **FP-LMTO has been extensively used to understand mechanical properties of the $d-$ and $f-$electron systems (Söderlind; for Ta 1998).**

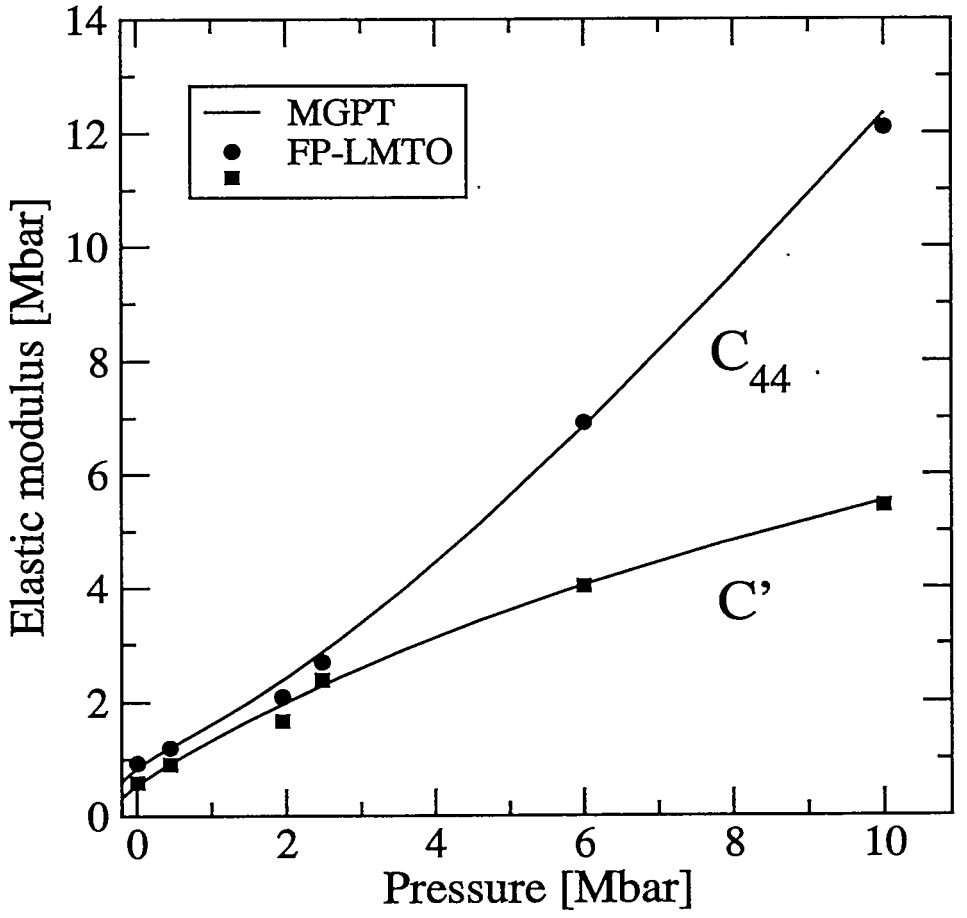
⇒ **Ion thermal contribution is calculated via model generalized pseudopotential theory(MGPT) (Moriarty, 1990,1994):**

- **multi-ion interatomic potentials based on generalized pseudopotential theory(GPT) (Moriarty, 1988)**
- **volume dependent, but *structurally* independent**
- **a transferrable potential for transition metals**
- **validated on many d-transition metals, for Ta (Yang et al., 2001)**
- **based on FP-LMTO at T = 0 K and ambient experimental data**

⇒ **These two methods were coupled over a (Ω, T) grid for pressure and the elastic moduli.**

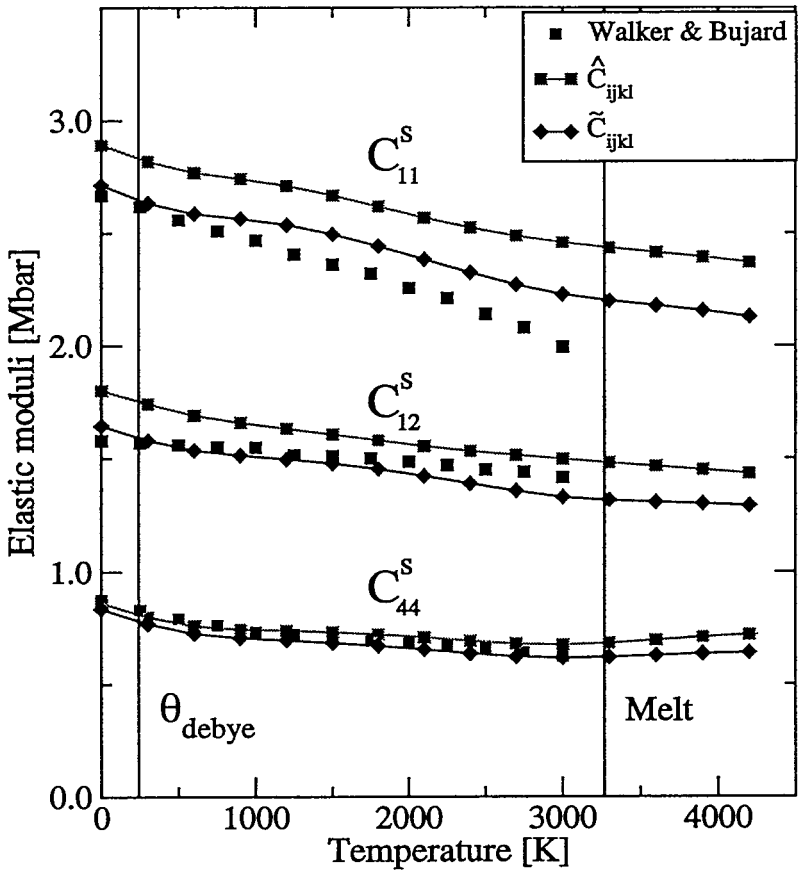
Ta: MGPT elastic moduli fitting

T = 0 K



- **MGPT is based on FP-LMTO results at T = 0 K with additional information from experiment.**

Ta: Elastic moduli temperature dependence



	C_{11}	C_{12}	C_{44} [Mbar]
Present theory	**2.72**	**1.65**	**0.83**
Walker & Bujard	**2.67**	**1.58**	**0.88**

	Θ_D[K]	γ
Present theory	**226**	**1.69**
Woods	**226**	**-**
Katahara *et al.*	**-**	**1.64**

- **This is at ambient pressure.**
- **The largest contribution to temperature dependence is due to thermal expansion.**

Notation

- **Either of these methods can be used to calculate the cold contribution C^o_{ijkl}.**

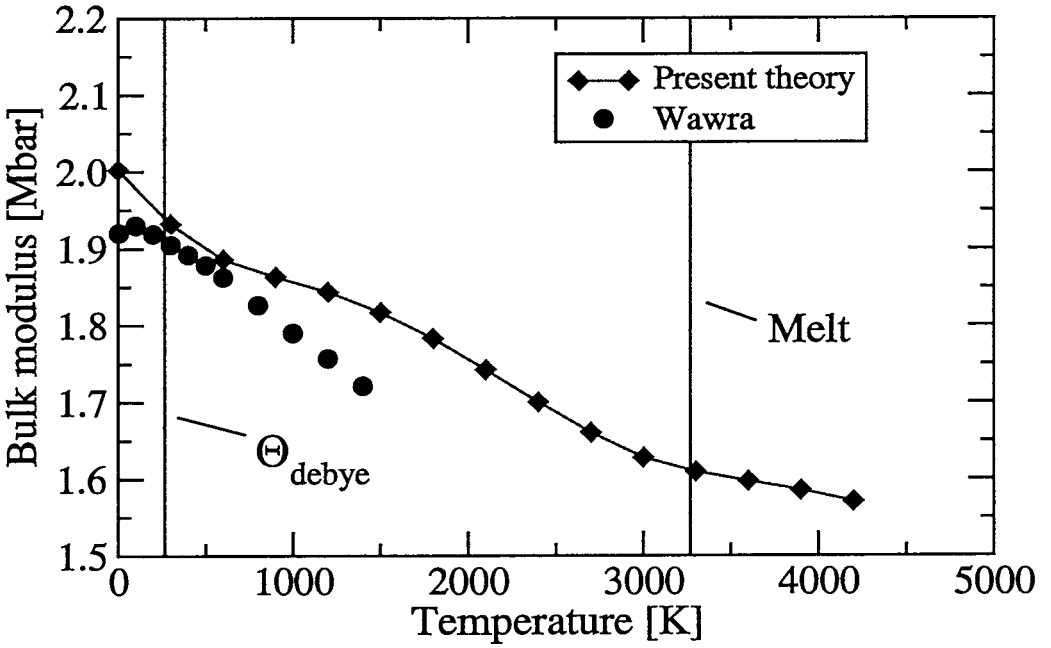
- **Therefore, for presentation purposes, we denote the method used to calculate the cold contribution in the following manner: $\widehat{C}_{ijkl}$ symbolizes that the FP-LMTO method was used for both the cold and the electronic-thermal contributions leaving the ion-thermal part being calculated via MGPT; similarly, $\widetilde{C}_{ijkl}$ symbolizes that the MGPT method was used for both the cold and the ion-thermal part leaving electron-thermal part being calculated via FP-LMTO.**

NB To compare with experiment, the adiabatic elastic moduli are related to isothermal elastic moduli by the following relation,

$$C^S_{ijkl} - C^T_{ijkl} = \frac{T}{\Omega C_\eta} \left.\frac{\partial \tau_{ij}}{\partial T}\right|_\eta \left.\frac{\partial \tau_{kl}}{\partial T}\right|_\eta .$$

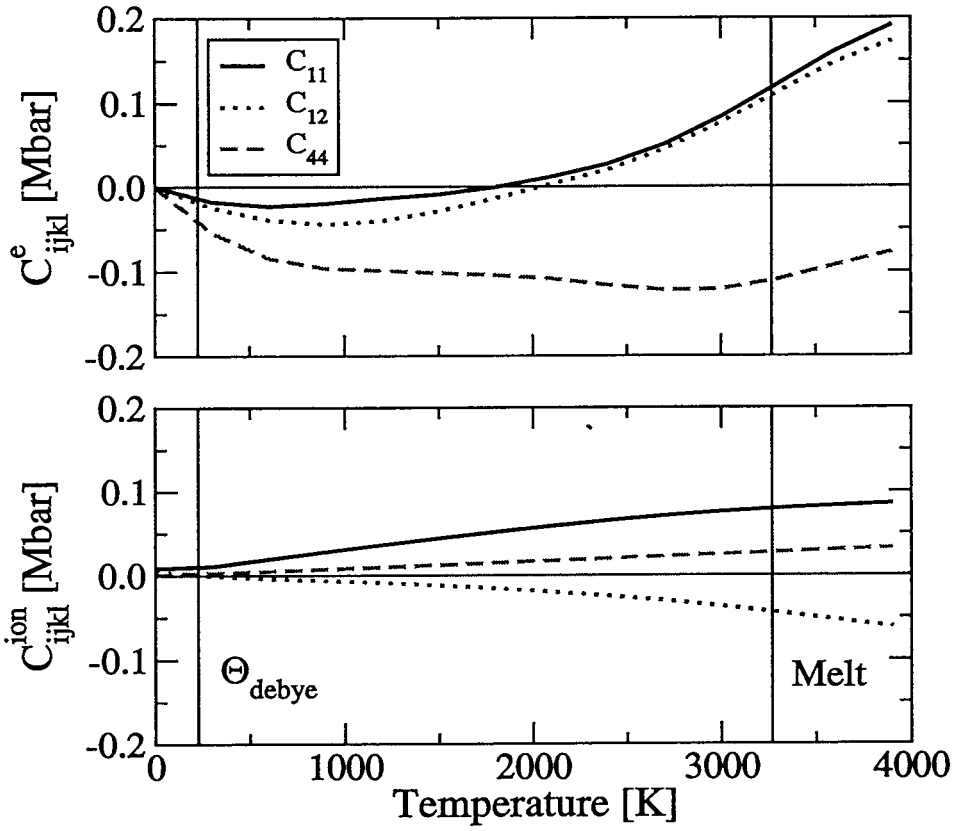
Ta: Bulk modulus temperature dependence

- **This is at ambient pressure.**



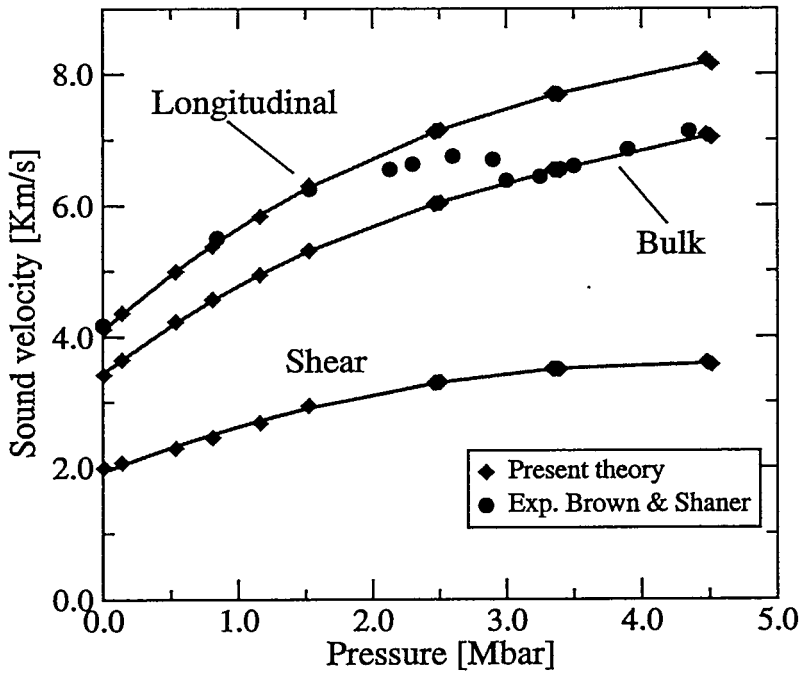
	K^S @ T = 300 K
Present theory	**1.93**
Wawra	**1.91**
Katahara et al.	**1.96**

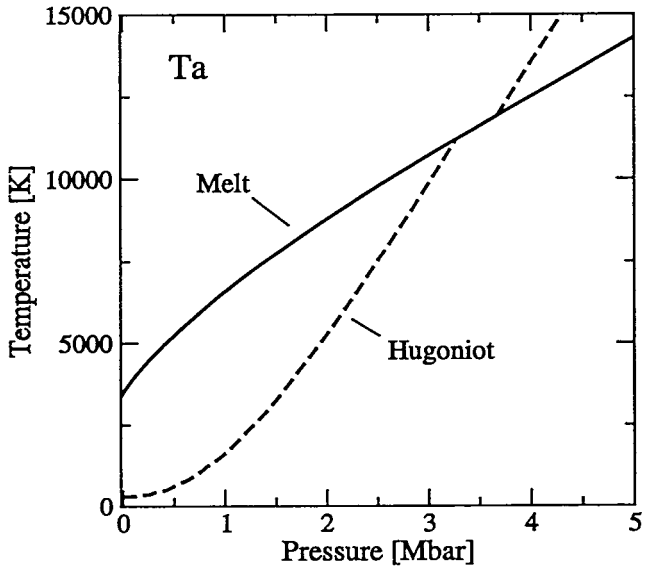
Elastic moduli contributions



- **At ambient pressure, the electron and ion thermal contributions are plotted separately.**

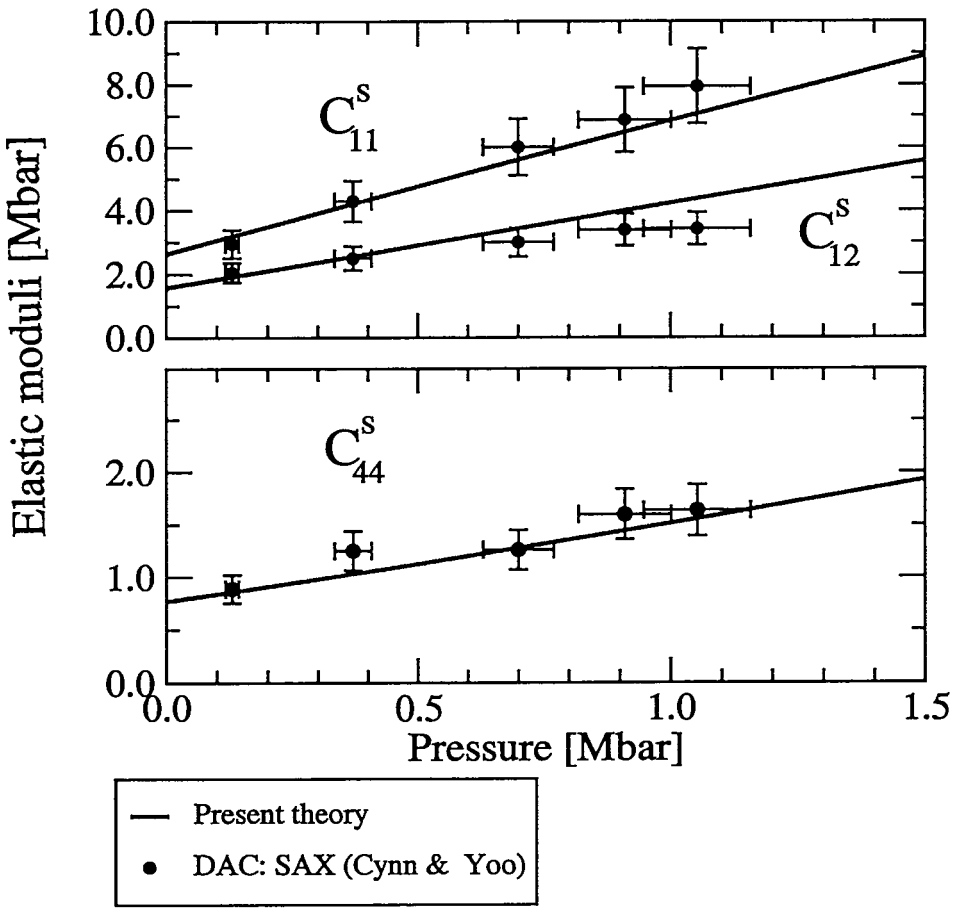
Ta: Sound velocity along the Hugoniot





- **Hugoniot is a locus of end states due to a single shock wave.**
- **The aggregate sound speed is the averaged bounds from the Hashin-Shtrikman estimate.**

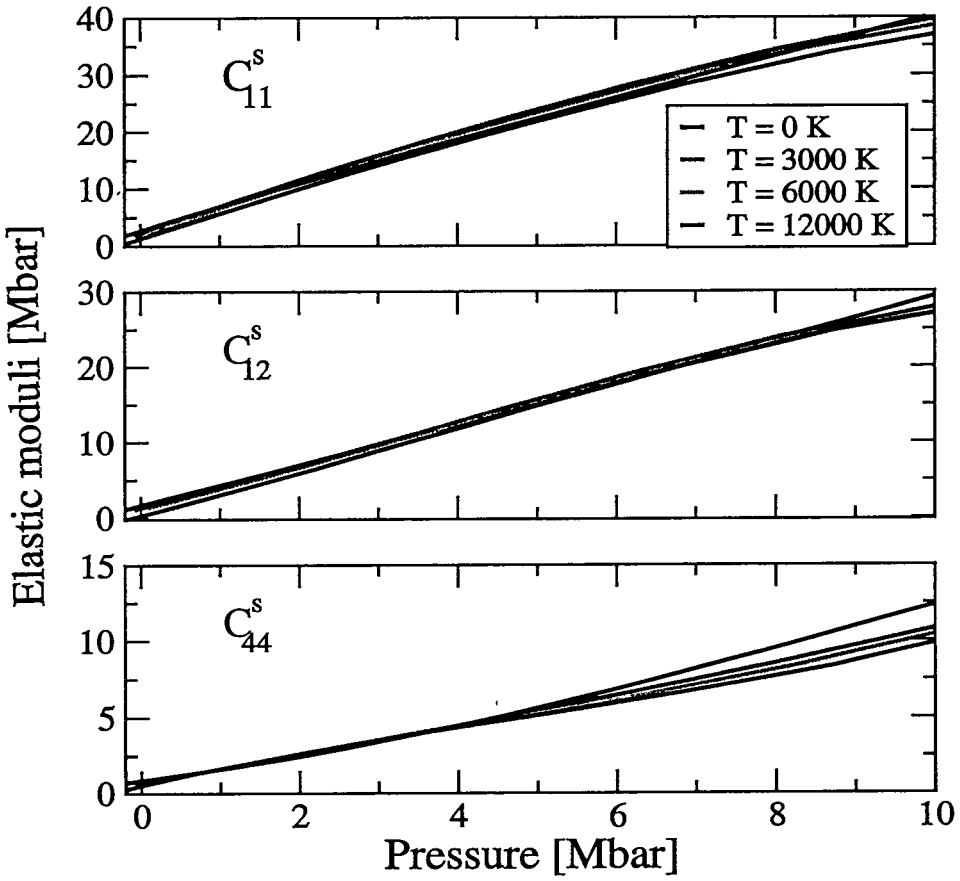
Ta: Elastic moduli pressure dependence



- **This is at ambient temperature.**

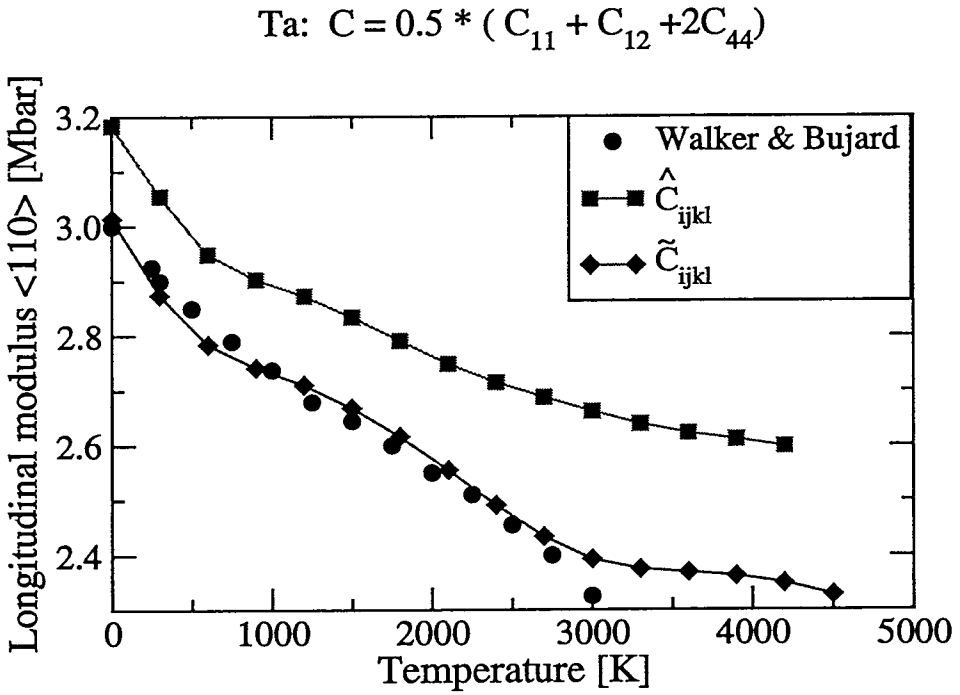
Ta: Elastic moduli

- **Calculated pressure dependence at several temperatures**

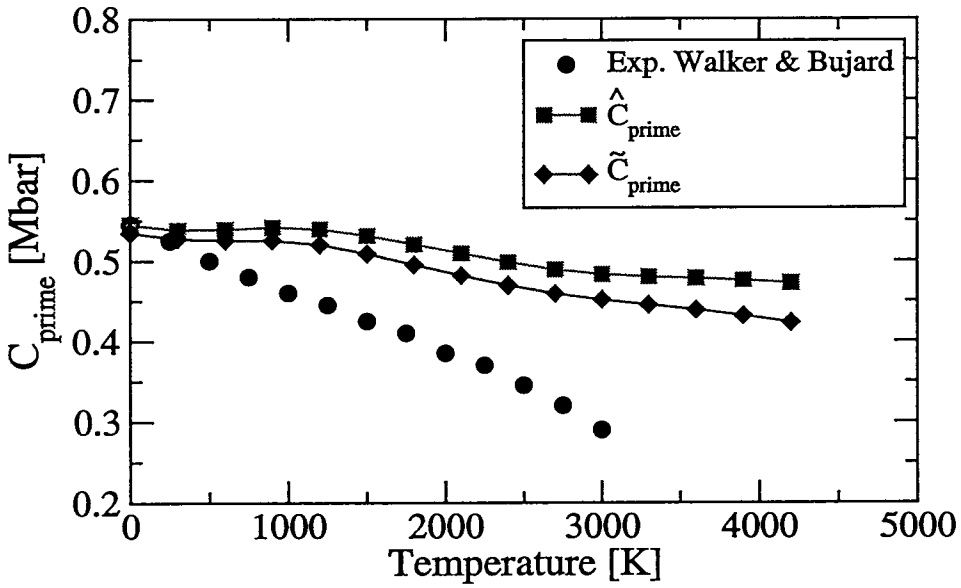


- **A general softening is observed for the elastic moduli at high pressure due to temperature.**

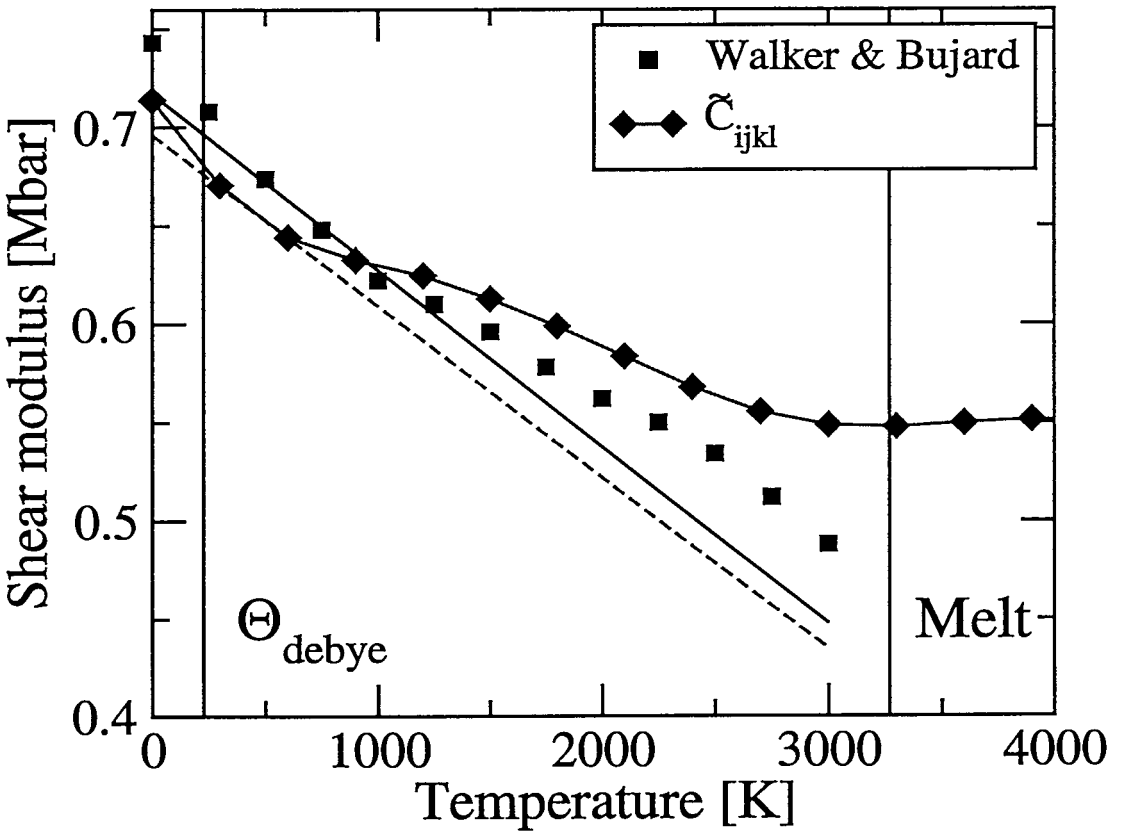
Ta: Longitudinal modulus



Ta: Shear modulus



Steinberg-Guinan model: temperature dependence



- **A Voigt average was used here**

$$G_v(P,T) = 1/5\left[2C'(P,T) + 3C_{44}(P,T)\right]$$

- **Using the Hashin-Shtrikman estimate for the shear modulus, we obtained similar results.**

Steinberg-Guinan Model

- **In general, the Steinberg-Guinan model is**

$$G = G_o \left[1 + \frac{1}{G_o} \frac{dG}{dP} \frac{P}{\eta^{1/3}} + \frac{1}{G_o} \frac{dG}{dT} (T - 300) \right]$$

where G_o is G at P = 0 and T = 0 and where $\eta = \Omega/\Omega_o$ (Steinberg, et al. 1980).

- **Hence,**

$$G(P = 0, T) = G_o \left[1 + \widetilde{A} (T - 300) \right]$$

where $\widetilde{A} = 1/G_o(dG/dT)$ is evaluated at zero pressure and T = 300 K. For the shear modulus G, we use a Voigt average, $G_v(P,T) = 1/5 \left[2C'(P,T) + 3C_{44}(P,T) \right]$.

- **The shear modulus constant G_o from the SG model for Ta has a value of 0.69 Mbar, and from our values we obtain similar results of 0.69 and 0.67 Mbar for the FP-LMTO and MGPT, respectively. Also, for $\widetilde{A}_v$, the SG model gives -0.13 [kK]$^{-1}$, which is comparable to our results of -0.11 [kK]$^{-1}$ (FP-LMTO) and -0.13 [kK]$^{-1}$ (MGPT).**

Sound velocity

- **For isotropic polycrystalline Ta, the estimated aggregate sound speed is performed by averaging the bounds g_1 and g_2 of the Hashin-Shtrikman estimate(Simmons,1971) for shear:**

$$v_l = \sqrt{(K_s + 4g_{ave}/3)/\rho}$$

$$v_b = \sqrt{K_s/\rho}$$

$$v_s = \sqrt{g_{ave}/\rho}$$

$$g_1 = C' + \frac{3}{\frac{5}{C_{44} - C'} - 4\beta_1}$$

$$g_2 = C_{44} + \frac{2}{\frac{5}{C' - C_{44}} - 6\beta_2}$$

where

$$\beta_1 = -3\frac{K_s + 2C'}{5C'(3K_s + 4C')}$$

$$\beta_2 = -3\frac{K_s + 2C_{44}}{5C_{44}(3K_s + 4C_{44})}$$

Conclusions

- **Within the quasi-harmonic approximation, the thermoelastic properties of bcc Ta were investigated for temperatures up to 12,000 K and for pressures up to 10 Mbar.**

- **Both *ab initio* FP-LMTO and model generalized pseudopotential(MGPT) theories were combined to account for the electron-thermal and ion-thermal contributions.**

- **Calculated elastic moduli results agree with experiments for**
  - **the temperature dependence at ambient pressure,**
  - **the pressure dependence at ambient temperature,**
  - **and aggregate sound velocities in high pressure shock systems.**

⇒ In the future, we intend to account for anharmonic thermal ion contributions to the elastic moduli.

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